

**INTERFERENCES AFFECTING THE ANALYSIS
OF ALUMINUM IN WATERS BY
SOLVENT EXTRACTION-ATOMIC ABSORPTION
SPECTROMETRY: A Comparison of
Two Solvent Extraction Procedures
Using the Oxine-MIBK System**





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SOLVENT EXTRACTION-ATOMIC ABSORPTION SPECTROMETRY:
A COMPARISON OF TWO SOLVENT EXTRACTION PROCEDURES
USING THE OXINE-MIBK SYSTEM

by

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1 SUMMARY

Interference of thirteen, mainly divalent, metal ions on the analysis of aluminum in water by solvent extraction - atomic absorption spectrometry (SE-AAS) using the 8-hydroxyquinoline (oxine)-methyl isobutyl ketone (MIBK) system in two extraction procedures was studied. One procedure, in which the extraction was performed at pH 9, is detailed in "Standard Methods for the Examination of Water and Wastewater"; while the other in which the extraction was performed at pH 8 is detailed in Environment Canada's method and in the method of the Water Analysis Laboratory (WAL) at the Alberta Environmental Centre (AEC).

Testwork on 0.5 mg/L Al (mid-range) solutions identified interferences from Cr(III), Fe(III) and Mn(II) with a more severe effect exhibited at pH 8 than at pH 9. Al recovery at pH 8 is significantly decreased by the presence of 0.1 mg/L Cr(III) and declines to 15% at the 3 mg/L Cr(III) level. At pH 9, the Cr(III) interference effect is not as marked, beginning at 3 mg/L Cr(III) and yielding a 75% Al recovery at a concentration of 10 mg/L Cr(III). In the case of Fe(III) interference at pH 8, Al recovery begins to decrease at the 1 mg/L Fe(III) level and is reduced to 35% at the 20 mg/L Fe(III) level. At pH 9 the Fe(III) interference effect is less marked, beginning at the 5 mg/L Fe(III) level and decreasing Al recovery to 75% at the 20 mg/L Fe(III) level. Mn interfered in both procedures above the 50 mg/L level. There was no interference for either procedure from Cd, Co, Cr(VI), Cu, Ni, Pb and Zn up to 1 mg/L level tested, and from Ba, Mo, and V up to the 10 mg/L level tested. Also there was no interference from Mg up to the 500 mg/L level tested, if the extraction was performed immediately after the addition of oxine.

The Cr(III) interference identified in this study appears to be undocumented in the literature. At low Al levels the Fe(III) and Mn interference at pH 9 found in this study occur at concentrations lower than stated in the published methods (5 mg/L Fe rather than 10 mg/L Fe and 50 mg/L Mn rather than 80 mg/L Mn).

2 INTRODUCTION

Solvent extraction of a metal chelate and subsequent determination by atomic absorption spectrometry (SE-AAS) has been utilised by analysts to determine trace metal concentrations in water for over 25 years. The advantages of preconcentration, increased sensitivity, matrix uniformity and the elimination of a number of interferences are well known [1-6].

Trace aluminum in waters can be determined by chelation with oxine and extraction into solvents such as chloroform [7-10], ethyl propionate [2, 3, 11] or MIBK [12-21]. One method consisting of an oxine chelation and MIBK extraction at pH 8 followed by analysis by atomic absorption spectrophotometry [13, 20] was implemented at WAL as a routine analytical method in 1989. This will be subsequently referred to as Method I. Many laboratories use a similar procedure (Method II) which is described in "Standard Methods for the Examination of Water and Wastewater" [12]. Although these two procedures both involve the formation of aluminum (III) oxinate, extraction into MIBK and measurement by AAS, they differ in extraction pH (8 or 9) and the sequence of reagent addition. Figure 1 illustrates the differences.

Heavy metal ion interferences with the oxine - MIBK system have been evident [12-14, 16, 17, 19, 21]. Habib et al. [14] referred to interferences associated with Method I. They found that there was significant interference from concentrations greater than 0.1 mg/L of a composite solution containing Cu(II), Pb(II), Cd(II), Zn(II), Fe(III) and Cr(VI). However, a selective study to determine which ion or ions interfered was not undertaken. The Standard Methods procedure [12] and Environment Canada's procedure [13] both state that Fe over 10 mg/L and Mn over 80 mg/L will interfere.

Our experience from interlaboratory studies, from laboratory samples and from related investigations involving direct current plasma atomic emission spectroscopy (DCP-AES) [21] indicates the existence and the extent of the interferences in Method I may be more severe than documented. Table 1 shows aluminum results 25-43% lower than design values for seven of the samples received in two interlaboratory round robin studies initiated by the Alberta Water Analyst's Committee (AWAC) and one interlaboratory study from the Environment Canada Ecosystems Interlaboratory QA Program (FP). The levels of heavy metals present are such that one of them or a combination of them could have caused interference in the aluminum determination.

It has been observed that Al recoveries for a few unfiltered, preserved laboratory samples analysed by Method I have been lower than those from an aqua regia digestion - inductively coupled argon plasma spectrometry (ICAP) method. It is difficult to draw any firm conclusions regarding possible interferences from this data since the aqua regia digestion - ICAP method determines not only the soluble Al, but also Al that may be dissolved from any sediment in the sample, while Method I determines only Al in solution that is available for chelation. Insufficient

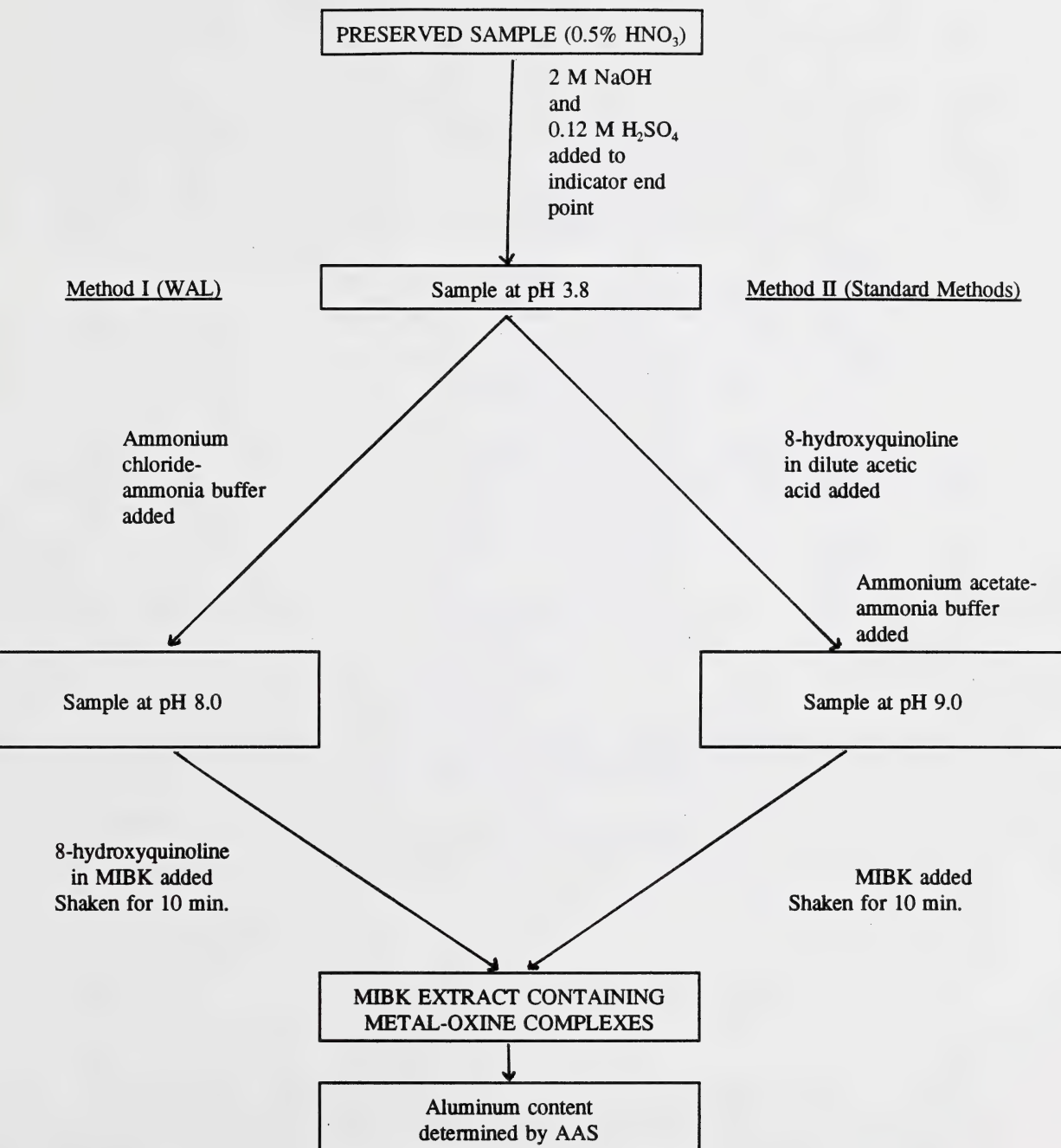


Figure 1. Comparison of Method I and II procedures.

Table 1. Low recovery of aluminum determined by SE-AAS Method I compared with design or mean values of interlaboratory study samples containing various levels of heavy metals

Interlab Study	Sample #	Al SE-AAS Method I		Design or Mean* Concentrations (mg/L)											
		% Recovery (SE-AAS)/ Design Or Mean	Measured Concentration (mg/L) (SE-AAS)	Al	Fe	Mg	Cr	Cu	Zn	Cd	Co	Ni	Mn	V	Mo
AWAC 21	6	75	0.494	0.656	0.675	-	0.938	1	1.25	0.119	0.312	0.125	0.106	0.969	0.688
AWAC 25	3	73	0.924	1.26	9.95	15	0.54	0.747	1.72	3.69	0.199	2.45	0.172	0.586	0.583
AWAC 25	4	63	1.37	2.17	9.87	14	1.11	1.59	2.99	3.66	0.486	4.45	0.455	1.28	1.38
AWAC 25	7	57	0.157	0.274	0.158	<1	0.774	0.204	0.099	0.14	0.19	0.326	0.176	0.24	0.099
FP63	8	75	0.180	0.240	0.327	30	0.368	0.200	0.177	0.270	0.172	0.340	0.144	0.442	0.202
FP63	9	73	0.349	0.480	0.281	12	0.442	0.443	0.542	0.170	0.391	0.370	0.222	0.332	0.460
FP63	10	70	0.703	1.00	0.502	23	0.100	0.100	0.106	0.096	0.288	0.483	0.100	0.958	0.955

* Mean value from 17 laboratories available for AWAC 25, samples 3 and 4; and from 28 laboratories for FP63 samples 8-10.

- Data not available.

sample volume after routine analysis requirements have precluded further investigation of such samples.

During the development of an automated solvent extraction DCP-AES system for the determination of aluminum [21] an interference study was performed. With Method I conditions for the chelation/extraction step the interferants were found to be Cr(III), Fe(III), Mn(II), and Ni(II) and with Method II conditions they were Cr(III), Fe(III), and Mg(II).

With all this evidence in mind this study was planned to investigate the possible interference effects of the heavy metals, Fe, Cr, Mg, Mn, Cd, Cu, Pb, Zn, V, Mo, Co, Ni and Ba at various concentrations on the determination of aluminum by both Method I and II.

This study aims to provide a better understanding of the interference sources so that low aluminum recoveries may be explained, possible method modifications may be implemented, and to provide information to facilitate the selection of aluminum results when these are available from other methods or to flag results when known interferants are present.

3 EXPERIMENTAL

3.1 Atomic Absorption Spectrophotometer

A Perkin Elmer Model 603 atomic absorption spectrophotometer was employed in conjunction with an aluminum hollow cathode lamp and a nitrous oxide burner head. The spectrometer was connected to a Technical Marketing Associates strip chart recorder. The 309.3 nm spectral line was used and the burner height adjusted to setting 14. The lamp current was 25 mA and the slit width was 0.7 nm. Flowmeter settings were 75 (delivery pressure 10 psig) for acetylene and 60 (delivery pressure 20 psig) for nitrous oxide. The sample flow rate was 7.0 mL/min.

3.2 Procedure

Experimental details concerning chemicals, reagents, sample preparation and instrument operation are adequately covered in the AEC method [15] referred to as Method I, and the "Standard Methods for the Examination of Water and Wastewater" [12], referred to as Method II. (These methods are included in Appendices A and B.)

One modification made to Method II was that all the test solutions were brought to the same pH of 3.8 (red end point with methyl red/bromophenol blue indicator) prior to chelation. This is an integral part of Method I since water samples, although uniformly preserved, come from a wide range of sources and do not necessarily arrive in the laboratory with identical pH.

The ammonium acetate - ammonia buffer employed in Method II has a pH of 9.5 ± 0.1 . When 10 mL of this buffer is added to a sample at pH 3.8 with the appropriate volume of oxine solution present, the resulting pH is 9.0 ± 0.1 .

3.3 Interference Study Solutions

For each part of the study a blank solution, a 0.5 mg/L aluminum solution and solutions containing 0.5 mg/L aluminum plus various concentrations of interfering ions were prepared. Solutions were made up in 500 mL glass volumetric flasks previously soaked for at least 1 day in 10% HNO_3 solution and rinsed three times with ASTM type I water obtained directly from a NANOpure water purification system fed with distilled water.

To provide a 0.5% HNO_3 matrix in the final solution, 2.5 mL of concentrated reagent grade HNO_3 were added to each flask. This matches the preservation requirements for samples entering the laboratory for heavy metal analysis.

A set of six standards containing 0.1 and 1.0 mg/L aluminum plus 1, 5 and 10 mg/L Cr(III) were prepared in a similar manner to further investigate Method II.

A composite sample, prepared from several preserved industrial effluent samples, was divided and spiked with Cr(III) and Fe(III) standard solutions to produce final concentrations of 1 and 5 mg/L Cr(III) and 2 and 6 mg/L Fe(III). These spiked samples were used to check aluminum recoveries within a sample matrix. The unspiked sample was analysed by an ICAP method and found to contain 0.27 mg/L Al, 0.01 mg/L Cr, 0.37 mg/L Fe, 35 mg/L Mg and 0.10 mg/L Mn.

Aluminum and other heavy metal constituents were obtained from 1000 mg/L ICAP standard solutions (High Purity Standards; Charleston, SC) or equivalent (an exception was the 1000 mg/L magnesium solution which was a purchased atomic absorption standard). Gilson P1000 and P200 micropipettors were utilised to dispense the appropriate volumes of these standards. Standard solutions were brought to a final volume of 500 mL with ASTM type I water.

Care was taken throughout the preparation of these standard solutions and the composite sample to minimize any possible contamination.

All standard solutions were stored in clean 500 mL polyethylene bottles.

3.4 Reagents

Concentrated nitric, sulphuric and acetic acids and concentrated ammonium hydroxide were reagent grade. The MIBK was atomic absorption spectroscopy grade. All reagent chemicals were reagent grade.

4 RESULTS AND DISCUSSION

The results for the main interfering metals identified during this interference study are presented and discussed below.

4.1 Chromium(III) Interference

Method I exhibits a rapid and immediate decrease in aluminum recovery as the Cr(III) concentration increases (Figure 2). There is close to a 60% reduction in recovery at the 1 mg/L Cr(III) level. This trend in the data is in agreement with that obtained from studies conducted on an automated solvent extraction system, based on Method I, connected to a DCP-AES instrument [21]. In a manual simulation of this procedure, involving back extraction with 5% HNO₃ prior to aspiration into the DC plasma, a 70% reduction in recovery of a 0.5 mg/L Al solution was observed at the 1 mg/L Cr(III) level. Thus it is evident that the interference is independent of the instrumental analytical step (AAS or DCP-AES) and must occur during the chelation-extraction process.

Method II is also affected by Cr(III) but not to as great an extent as Method I. The recovery is 100% up to 2 mg/L Cr(III) and the decline not as abrupt, giving a 25% reduction in recovery at the 10 mg/L Cr (III) level. Since this interference is not documented in the literature further tests were conducted at the 0.1 mg/L and 1.0 mg/L aluminum levels. The recovery data is detailed in Figure 3.

Al recovery data on a Cr(III) spiked combined industrial effluent sample (Figure 4) showed the same trend for Method I and II as exhibited by the Cr(III) spiked 0.5 mg/L Al standard. However the interference for both methods is more severe. This may in part be due

to the contributing interference from Fe(III) already present in the combined sample at a concentration of 0.37 mg/L.

Wu et al. [21] found that Cr(III) was not extracted into MIBK at pH 8 and this is supported by Onishi's [9] and Sary's [10] observations that Cr(III) is not extracted in an oxine-chloroform system. Hence interference due to competition for oxine between chromium (III) and aluminum is unlikely.

The fact that the level of interference in the two methods differs is linked either to the extraction pHs being different (8 or 9) and/or the sequence of oxine and buffer solution addition. At pH 8 the presence of Cr(III) may enhance the hydrolysis of aluminum and inhibit the formation of aluminum oxinate [22].

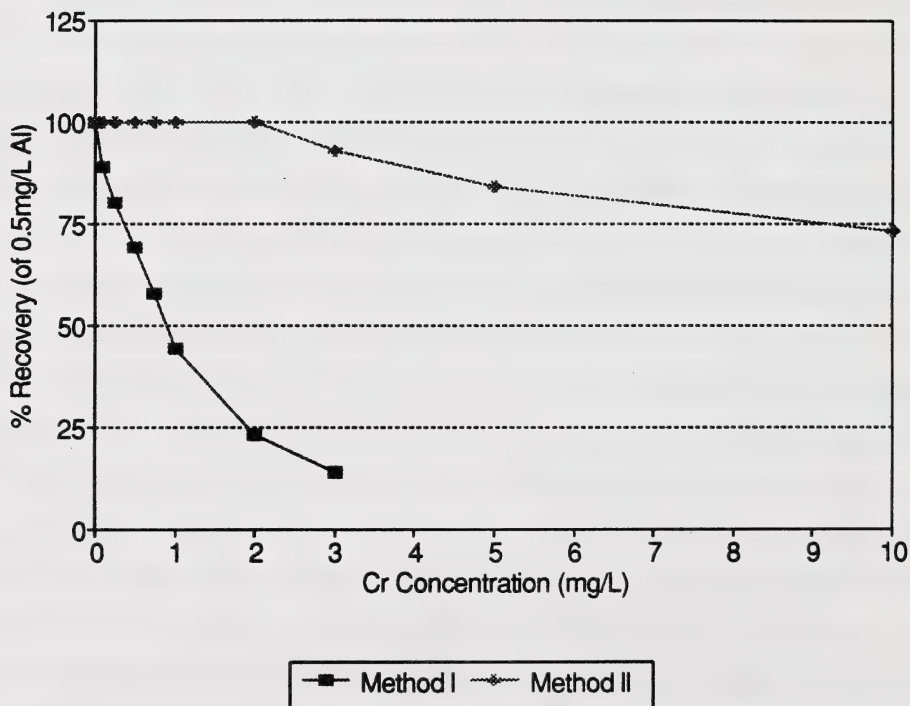


Figure 2. Recovery of 0.5 mg/L Al in the presence of increasing Cr (III) concentration.

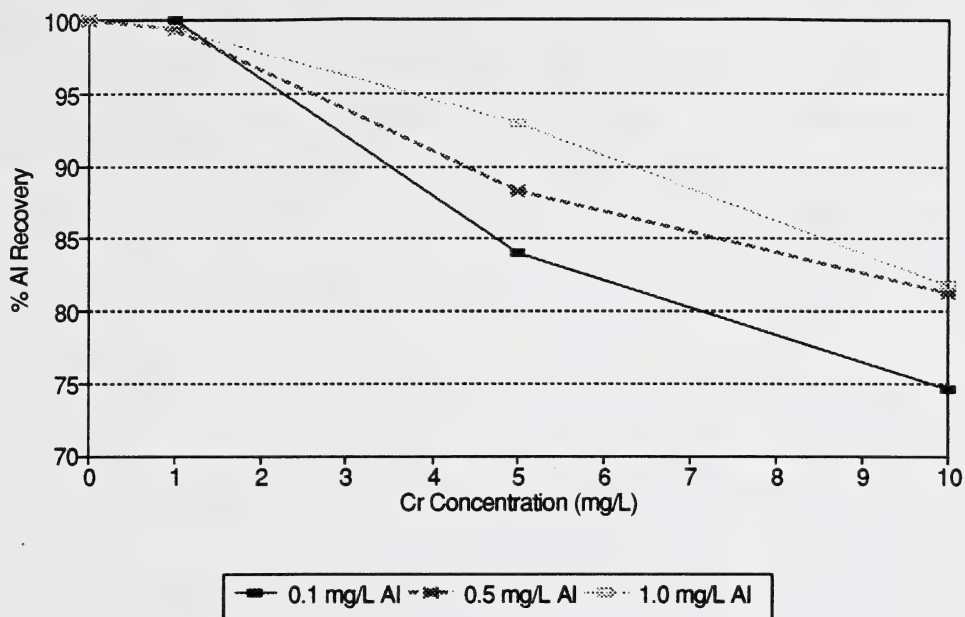


Figure 3. Comparison of Al recoveries for 0.1, 0.5 and 1.0 mg/L Al solutions containing 1, 5 and 10 mg/L Cr(III) determined by Method II.

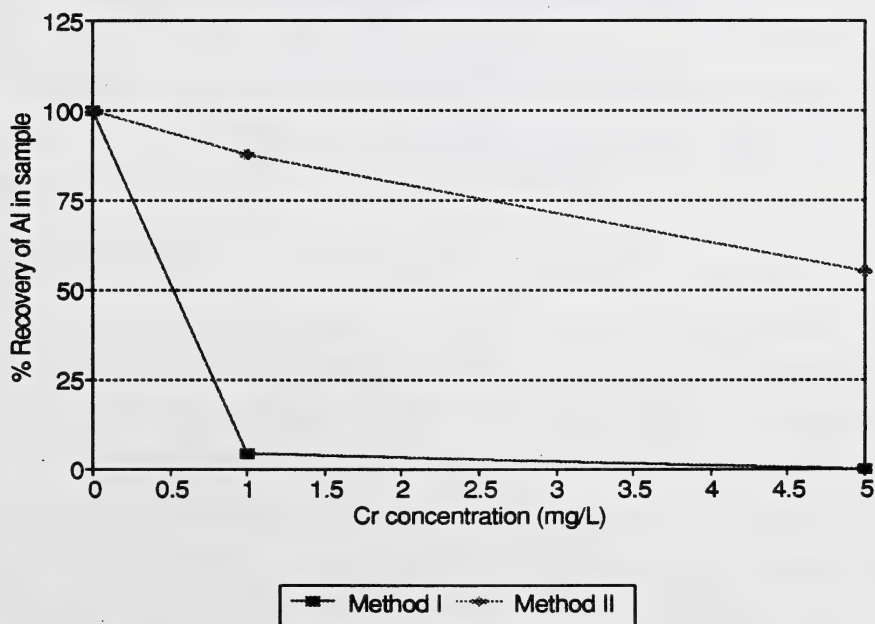


Figure 4. Al Recovery in composite sample spiked with Cr(III).

4.2 Iron(III) Interference

Both procedures were influenced by the presence of Fe(III). Figure 5 shows a significant decrease in aluminum recovery for Fe(III) concentrations over 1 mg/L for Method I and over 5 mg/L for Method II. On the whole the effect is not as pronounced for Method II as it is for Method I. In both cases the interference is probably linked to the formation of insoluble iron hydroxides.

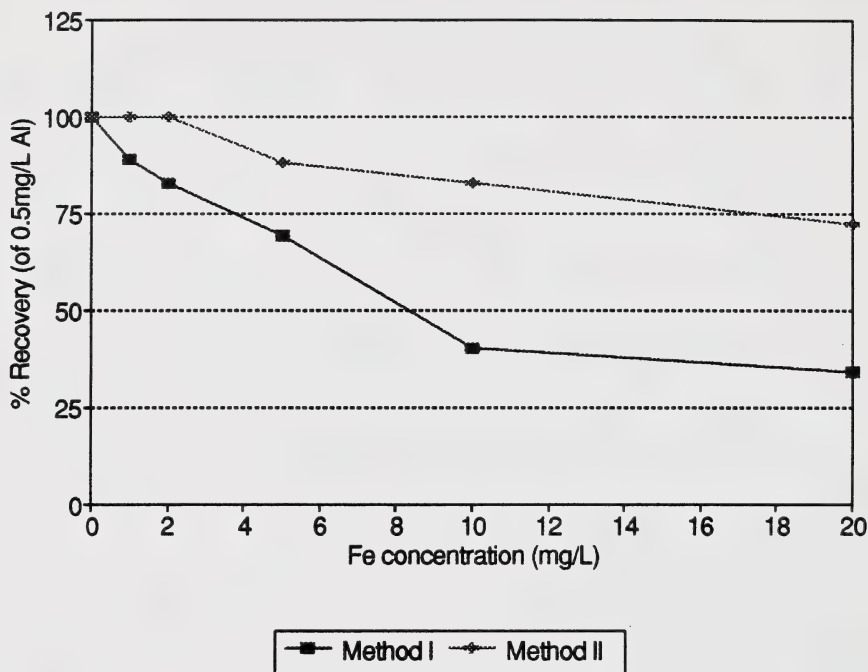


Figure 5. Recovery of 0.5 mg/L Al in the presence of increasing Fe (III) concentration.

Al recovery data on a Fe(III) spiked combined industrial effluent sample (Figure 6) showed the same trend for Method I and II as exhibited by the Fe(III) spiked Al standard.

Difficulty was encountered during the step to bring the solutions to pH 3.8. Those solutions containing more than 10 mg/L Fe(III) precipitated brown $\text{Fe}(\text{OH})_3$ when base was added and the indicator end-point was not discernible. This can be overcome by use of a pH meter. One with a 20 cm probe to accommodate 200 mL volumetric flask necks is most effective.

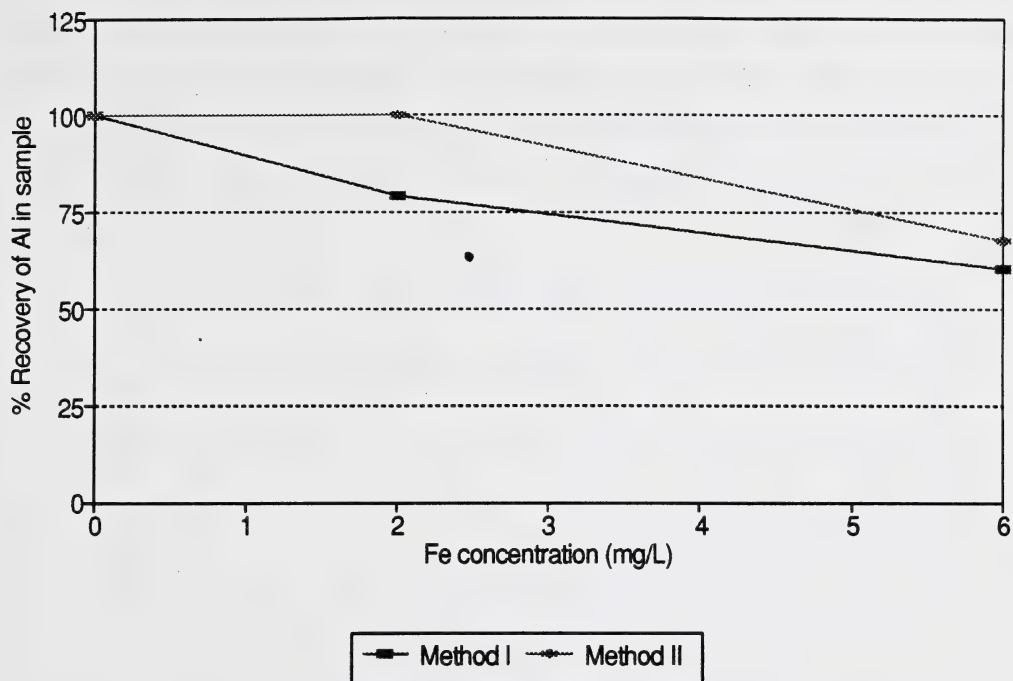


Figure 6. Al Recovery in composite sample spiked with Fe(III).

The literature states that Fe(III) interference can be eliminated by reducing the Fe(III) to Fe(II) using hydroxylamine hydrochloride and subsequently complexing the Fe(II) with 1, 10 phenanthroline [12, 17].

4.3 Manganese Interference

It was found that manganese does not interfere up to the 50 mg/L level in either Method I or II (Figure 7). Above this concentration the effect of manganese is greater for Method II than Method I. Since most water samples contain less than 5 mg/L Mn this interference is not a concern.

Some difficulty was encountered with both procedures due to the presence of manganese. Firstly the step bringing the pH to 3.8 was hindered in samples containing more than 5 mg/L Mn since the indicator was no longer effective due to the presence of brown manganese hydroxide precipitate. A pH meter was used to overcome this problem. Secondly a thick greenish-brown

precipitate formed on addition of buffer in solutions containing more than 20 mg/L Mn in Method II. This precipitate persisted through the MIBK extraction step and produced a colloidal extract which did not settle. Stirring the extracts with a clean, glass rod and allowing them to sit for 15 minutes, covered, produced extracts that could be aspirated into the flame.

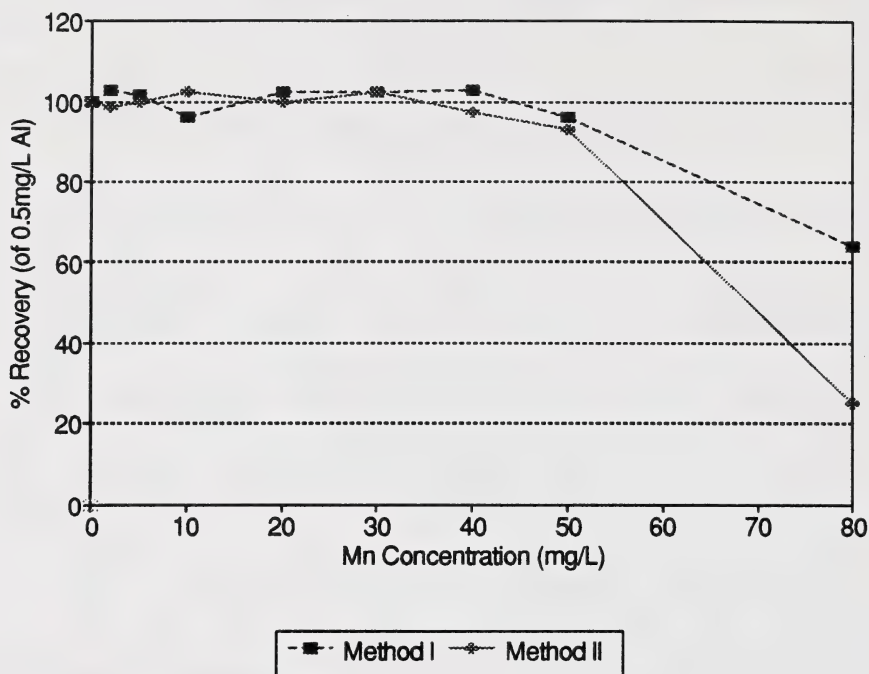


Figure 7. Recovery of 0.5 mg/L Al in the presence of increasing Mn concentration.

4.4 Magnesium Interference

The "Standard Methods for the Examination of Water and Wastewater" procedure [12] explains how magnesium is an interferant in this method and how to minimize its effect. Magnesium ions will chelate with oxine above pH 8 to form a pale green precipitate of magnesium oxinate. Aluminum is coprecipitated and not extracted into the MIBK. Fishman [16] states that as the pH increases from 8, the rate of magnesium oxinate precipitation increases. Since this precipitate begins to form within 3 - 6 minutes of the oxine and buffer solutions being added, it is recommended [12, 16] that immediate extraction of the solution with MIBK is done after this step.

In order to test Method II, oxine and buffer solutions were added to 0.5 mg/L Al solutions containing from 0 to 500 mg/L Mg. After swirling to mix, the solutions were allowed to sit for 10 minutes to provide the opportunity for magnesium oxinate to form. This was done to obtain a measure of the magnitude of the magnesium interference. At pH 9 these test solutions showed a visible pale green precipitate but no reduction in aluminum recovery occurred (Figure 8, Method II).

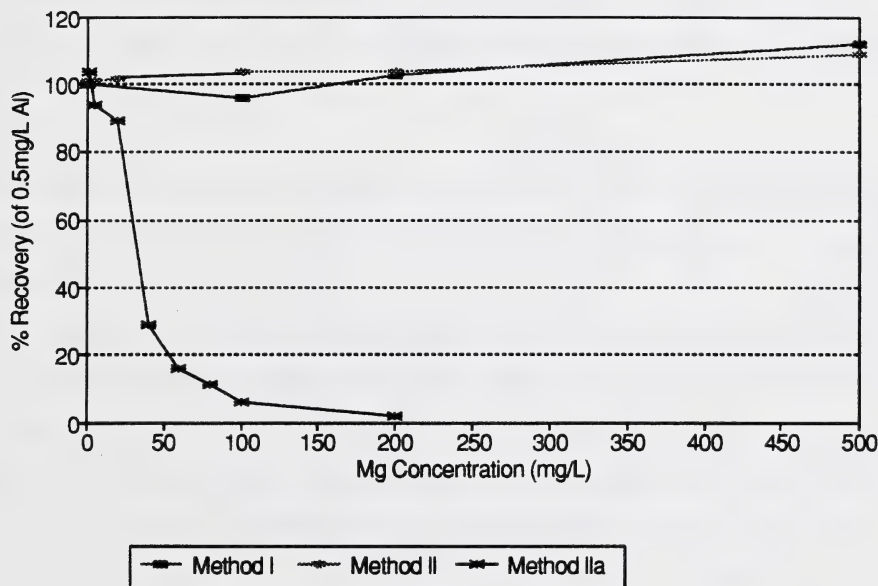


Figure 8. Recovery of 0.5 mg/L Al in the presence of increasing Mg concentration.

It was found that a 10 minute vigorous shaking on the automatic shaker immediately after oxine and buffer solutions addition (but before MIBK addition) promoted the formation of magnesium oxinate. The test was repeated with this modification. Precipitation was visible in volumes approximately proportional to magnesium concentration and in greater volume than had been observed previously. After extraction with MIBK the precipitate settled at the interface between the solvent and aqueous layers and care was taken not to aspirate it into the flame. A marked reduction in aluminum recovery was obtained as can be seen in Figure 8 (Method IIa referring to the data from this test).

These tests showed that although magnesium does interfere in this procedure, its effect can be eliminated by (1) minimizing sample agitation after initial gentle mixing with the oxine and buffer solutions and (2) extracting with MIBK within 10 minutes of buffer addition.

Magnesium, up to the 500 mg/L level, does not interfere when Method I is used (Figure 8, Method I). Magnesium oxinate does not have the opportunity to form since the oxine is not available until the extraction step (oxine is dissolved in MIBK).

The slight increase in aluminum recovery in Methods I and II is due to aluminum present as an impurity in the magnesium standard solution.

4.5 Other Heavy Metal Interferants

No reduction in the aluminum recovery of a 0.5 mg/L Al in 0.5% HNO₃ solution was encountered by either Method I or II for the following: a) separate additions of Cr(VI), Cd, Cu, Pb, Zn, V, Mo, Co, Ni - all at the 1 mg/L level; b) the combination of the same elements - Cr(VI), Cd, Cu, Pb, Zn, V, Mo, Co, Ni - all at the 1 mg/L level; and c) separate additions of V, Mo, Ba - all at the 10 mg/L level. There was a 60% reduction in the aluminum recovery of a 0.5 mg/L Al in 0.5% HNO₃ solution by Method I with the addition of a combination of Cr(III), Cd, Cu, Pb, Zn, V, Mo, Co, Ni - all at the 1 mg/L level. This is comparable in magnitude to the effect, shown in Figure 2, when Cr(III) is the single interfering element.

5 CONCLUSION

Information garnered during this study provides an explanation of the low results for aluminum achieved at WAL by Method I on interlaboratory (Table 1) and some routine laboratory samples. Relatively high levels of iron and/or chromium in the AWAC and FP interlaboratory sample studies account for the low aluminum recoveries by SE-AAS.

This study has shown a more accurate SE-AAS determination of aluminum in water can be achieved by the following measures:

Firstly, the method described in the "Standard Methods for the Examination of Water and Wastewater" (Method II) should be used. Cr(III) and Fe(III) interference effects are less than those in Method I.

Secondly, in Method II, the agitation and time period (<10 minutes) between addition of buffer and extraction with MIBK should be minimized to eliminate possible magnesium interference due to the formation of magnesium oxinate. Also, a hydroxylamine hydrochloride/1,10-phenanthroline solution which complexes the Fe(III) should be added to samples containing Fe(III) higher than 5 mg/L Fe to eliminate or reduce Fe(III) interference as suggested in [12, 17].

Finally the analyst should be aware that water samples containing >2 mg/L Cr(III) and/or >50 mg/L Mn will exhibit a decreased aluminum recovery with this method. These levels of chromium (III) and manganese do not occur commonly in surface, groundwater or municipal sewage waters but are more probable in industrial holding ponds and effluents.

A draft method [23] was written and the method implemented at WAL on October 1st, 1993.

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Appendix A

Method I - Determination of low level aluminum in water from the Water Analysis Laboratory, Alberta Environmental Centre (unpublished, 1989).

Aluminum, Extractable (Solvent Extraction, AAS Method)

Introduction

Aluminum is the most abundant metal found in the earth's crust (8.1%) but is never found in the free metallic form in nature. It occurs in minerals, rocks and clays and this accounts for the presence of aluminum in practically all natural waters as a soluble salt, a colloid or an insoluble compound. Potassium aluminum sulfate (kalimite) is used as a flocculation agent in water purification and generally accounts for elevated aluminum levels in treated water.

Summary of Method

Aluminum is complexed with 8-hydroxyquinoline at pH 8.0. Methyl isobutyl ketone is used to extract the aluminum-oxine complex from the aqueous phase. The solvent extract is aspirated into a nitrous oxide-acetylene flame in an atomic absorption spectrophotometer and the atomic absorption measured at 309.3 nm. The resulting absorption is compared against that of identically prepared aluminum standards.

Scope

This method can be used to determine aluminum in all fresh water and waste water samples. The range is from 0.005 to 1.0 mg/L Al and the detection limit is 0.030 mg/L Al. Higher concentrations may be determined by the appropriate dilution of samples.

Interferences

Testwork on this procedure has shown that chemical interferences occur due to the presence of heavy metal ions. There is a significant decrease in sensitivity as the sum of heavy metal constituents increases due to chelation competition effects.

Sample Container and Preservative

Samples are stored in polyethylene bottles and are preserved at pH <2 with 5 mL of 1+1 HNO₃ of sample.

Apparatus

1. Atomic absorption spectrophotometer
2. 200 mL volumetric flasks
3. Sample shaker
4. Recorder

Reagents

1. Buffer Solution (Ammonium chloride-ammonia): Dissolve 267.5 g NH_4Cl in 500 mL DDW and add 18.6 mL concentrated NH_4OH . Dilute to 1 L. The pH should be 8.0.
2. 8-hydroxyquinoline: Dissolve 3.75 g of 8-hydroxyquinoline ($8\text{-HO}(\text{C}_9\text{H}_6\text{N})$) in 500 mL MIBK.
3. Methyl isobutyl ketone (MIBK): Reagent grade (99.8% purity).
4. Sulphuric acid (0.125M): Dilute 7 mL of concentrated H_2SO_4 (96% purity) to 1 L with DDW.
5. Sodium hydroxide solution (2M): Dissolve 80 g NaOH in 800 mL DDW and dilute to 1 L when cool.
6. Indicator Reagent: Dissolve 0.25 g methyl red and 0.50 g bromophenol blue in 250 mL of anhydrous ethanol. Make up to 500 mL with DDW and mix thoroughly.
7. Stock Standard Aluminum Solution (1000 mg/L Al): Dissolve 1.000 g aluminum metal in 20 mL HCl with the addition of a trace of mercury salt to catalyse the reaction. Dilute to 1 L in a volumetric flask with DDW.
NOTE: A commercially prepared 1000 mg/L Al solution specified for atomic absorption analysis may also be used.
8. Intermediate Stock Standard Aluminum Solution (10 mg/L Al): Pipette 10 mL of the 1000 mg/L Al stock solution into a 1 L volumetric flask and add 5 mL of concentrated HNO_3 . Dilute to volume with DDW.
9. Working Standard Aluminum Solutions: Pipette appropriate volumes of 10 mg/L Al intermediate stock solution into 1 L volumetric flasks, add 5 mL of concentrated HNO_3 and dilute to volume with DDW.

<u>mL of 10 mg/L Al soln.</u>	<u>Working Standard Solution (mg/L) Al</u>
0	blank
2	0.020
5	0.050
10	0.100
20	0.200
50	0.500
100	1.000

10. Quality Control Stock Solution (1000 mg/L Al): A commercially prepared 1000 mg/L Al solution obtained from an alternate supplier to above may be used. Alternatively, aluminum metal from an alternative supplier to that used in (7.) may be used to prepare the QC stock solution as in (7.).
11. Quality Control Intermediate Aluminum Stock Solution (10 mg/L Al): Pipette 10 mL of the 1000 mg/L Al QC stock solution into a 1 L volumetric flask, add 5 mL concentrated HNO_3 and dilute to volume with DDW.
12. Quality Control Solution A (0.80 mg/L Al): Pipette 80 mL of the 10 mg/L Al QC intermediate stock solution into a 1 L volumetric flask, add 5 mL concentrated HNO_3 and dilute to volume with DDW.
13. Quality Control Solution B (0.20 mg/L Al): Pipette 20 mL of the 10 mg/L Al QC intermediate stock solution into a 1 L volumetric flask, add 5 mL concentrated HNO_3 and dilute to volume with DDW.
14. Quality Control Blank Solution (<0.005 mg/L Al): Add 5 mL of concentrated HNO_3 to a 1 L volumetric flask and dilute to volume with the same DDW as that used to prepare the other QC reagents.

Procedure

1. All samples should be preserved to pH <2.0 with HNO_3 at least 24 hr. prior to analysis.
2. Samples with visible turbidity may be filtered through a 0.45 μm membrane filter prior to analysis to prevent excessive emulsion formation.

3. Pipette 100 mL of samples and standards into individual 200 mL volumetric extraction flasks.
4. Add 4 drops of indicator solution and titrate to a blue endpoint with 2N NaOH solution.
5. Add 0.125M H_2SO_4 dropwise to bring the colour just back to red. At this point the solutions may be capped and analyzed the following day.
6. Add 10 mL $\text{NH}_4\text{Cl-NH}_3$ buffer solution to bring pH to 8.0. Mix thoroughly.
7. Add 8.0 mL of 8-hydroxyquinoline/MIBK solution to each flask and shake for 10 minutes. Let stand to settle for 5 minutes.
8. Float MIBK to top of flask neck by carefully adding DDW. In the event of an emulsion existing in the solvent layer a small plug of glass wool can be carefully inserted with a clean glass rod into the solvent layer to clarify it.
9. Analyze by atomic absorption within 2 hours. Adjust atomic absorption spectrophotometer according to prescribed instrument settings.

Glassware Handling

1. When analysis is completed, the remaining test solutions are poured into a separatory funnel in a fume hood. The aqueous portion can be discarded as non-hazardous waste. The organic phase must be disposed as a flammable toxic organic waste.
2. Using a test tube brush dipped in detergent solution, the neck of the flask is thoroughly brushed to remove solid residues.
3. Rinse the flask with DDW, then fill to within 1 cm of the top of the neck with 2% HNO_3 . Let stand for a minimum of 2 h. All glassware should be rinsed with DDW immediately before use.

Calculations and Method of Reporting

1. Prepare a calibration curve derived from the peak height readings of the standard solutions.
2. Determine the concentration of the metals by comparing the peak height readings of the samples with the standard curves.

Precision and Accuracy

1. In a single laboratory (Water Analysis and Research Branch), using a surface water, a sewage effluent and an industrial effluent at concentrations of 0.041, 0.203, and 0.099 mg/L of Al the coefficients of variation were 5.8%, 2.0%, and 4.0% respectively.
2. In a single laboratory (Water Analysis and Research Branch), using two EPA solutions with Al concentrations of 0.100 mg/L and 0.350 mg/L, the recoveries were 101% and 98%.

References

1. M.M. Habib, M. Voisard and E. Leitz, "Analysis of Aluminum by Chelation with 8-Hydroxyquinoline and Extraction into Methyl Isobutyl Ketone", Alberta Environmental Centre, Vegreville, Alberta, 1988.
2. "Standard Methods for the Examination of Water and Wastewater", American Public Health Association p. 164, 1985.

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Appendix B

Method II - Determination of low level aluminum in water from "Standard Methods for the Examination of Water and Wastewater". 18th Edition (1993).

3111 E. Extraction/Nitrous Oxide-Acetylene Flame Method

1. General Discussion

a. Application: This method is suitable for the determination of aluminum at concentrations less than 900 µg/L and beryllium at concentrations less than 30 µg/L. The method consists of chelation with 8-hydroxyquinoline, extraction with methyl isobutyl ketone (MIBK), and aspiration into a nitrous oxide-acetylene flame.

b. Interferences: Concentrations of Fe greater than 10 mg/L interfere by suppressing Al absorption. Iron interference can be masked by addition of hydroxylamine hydrochloride/1,10-phenanthroline. Mn concentrations up to 80 mg/L do not interfere if turbidity in the extract is allowed to settle. Mg forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to remove Al complex as a coprecipitate. However, the Mg complex forms slowly over 4 to 6 min; its interference can be avoided if the solution is extracted immediately after adding buffer.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

3. Reagents

a. Air: See 3111B.3a.

b. Acetylene: See 3111B.3b.

c. Ammonium hydroxide, NH₄OH, conc.

d. Buffer: Dissolve 300 g ammonium acetate, NH₄C₂H₃O₂ in water, add 105 mL conc NH₄OH and dilute to 1 L.

e. Metal-free water: See 3111B.2c.

f. Hydrochloric acid, HCl, conc.

- g. *8-Hydroxyquinoline solution*: Dissolve 20 g 8-hydroxyquinoline in about 200 mL water, add 60 mL glacial acetic acid, and dilute to 1 L with water.
- h. *Methyl isobutyl ketone*: See 3111C.3d.
- i. *Nitric acid*, HNO_3 , conc.
- j. *Nitrous oxide*: See 3111D.3h.
- k. *Standard metal solutions*: Prepare a series of standard metal solutions containing 5 to 1000 $\mu\text{g/L}$ by appropriate dilution of the stock metal solutions prepared according to 3111D.3k.
- l. *Iron masking solution*: Dissolve 1.3 g hydroxylamine hydrochloride and 6.58 g 1,10-phenanthroline monohydrate in about 500 mL water and dilute to 1 L with water.

4. Procedure

a. *Instrument operation*: See Sections 3111B.4b, C.4a, and D.4b. After final adjusting of burner position, aspirate MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent. Adjust wavelength setting according to Table 3111:I.

b. *Standardization*: Select at least three concentrations of standard metal solutions (prepared as in ¶ 3k) to bracket the expected metal concentration of a sample and transfer 100 mL of each (and 100 mL water blank) to four different 200-mL volumetric flasks. Add 2 mL 8-hydroxyquinoline solution, 2 mL masking solution (if required), and 10 mL buffer to one flask, immediately add 10 mL MIBK, and shake vigorously. The duration of shaking affects the forms of aluminum complexed. A fast, 10-s shaking time favors monomeric Al, whereas 5 to 10 min of shaking also will complex polymeric species. Adjustment of the 8-hydroxyquinoline to sample ratio can improve recoveries of extremely high or low concentrations of aluminum. Treat each blank, standard, and sample in similar fashion. Continue as in Section 3111C.4b.

c. *Analysis of samples*: Rinse atomizer by aspirating water-saturated MIBK. Aspirate extracts of samples treated as above, and record absorbances.

5. Calculations

Calculate concentration of each metal in micrograms per liter by referring to the appropriate calibration curve prepared according to ¶ 4b.

